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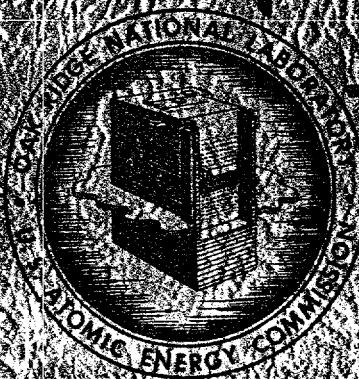
THE MTR-RaLa PROCESS FOR THE

PRODUCTION OF BARIUM-140

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
DIVISION OF UNION CARBIDE AND CARBON CORPORATION

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CHEMICAL TECHNOLOGY DIVISION

Laboratory Section

LABORATORY DEVELOPMENT OF THE MTR-RaLa

PROCESS FOR THE PRODUCTION OF BARIUM^{140}

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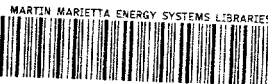
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2.0 Introduction

Kilocurie amounts of barium[140] have been produced in the Oak Ridge National Laboratory RaLa plant since 1945, using a precipitation process.[1,2] Originally, ORNL slugs were used as the raw material, but, as the required amount of product increased, it became more economical to utilize Hanford slugs. The RaLa plant was revised in 1950-51 to increase the safety of the equipment and to increase the plant capacity to 10,000 curies of barium[140] per batch.[3,4] In addition, the latter part of the RaLa precipitation process was replaced with an ion-exchange procedure to increase the purity of the product and to facilitate the handling of small amounts of material by remote control.[5-8]

Subsequently the consumer requested an increase in batch size to a minimum of 30,000 curies. Assemblies from the Materials Testing Reactor were proposed as the source for the production of the larger batches because of their high specific activity. An MTR assembly is composed of an aluminum-uranium[235] alloy, clad with pure aluminum, which after irradiation for 20 days would contain 3.88×10^4 curies of barium[140]. An economic survey[9] indicated that it would be cheaper to produce the larger batches in the ORNL RaLa plant using Hanford or Aiken slugs if the required production period was only two to three years. For a longer production period it was probably advantageous to install new RaLa processing facilities at the site of the Materials Testing Reactor.

In order to utilize MTR assemblies for the production of barium[140] it was necessary to develop a new RaLa process. The laboratory study of four possible chemical schemes is presented in this report. The development experiments were performed to scale in both glass and stainless steel equipment with 10- to 20-g transverse sections of a natural uranium MTR assembly, thus assuring the proper ratios of uranium and aluminum to silica and other impurities. The sections were irradiated in the X-10 graphite reactor to provide radioactivity for tracing the cations in the process. Inactive cations were added in the proper concentrations to represent the fission product masses. Cerium, or a mixture of cerium and lanthanum, was used to simulate the rare earths. The final process was chosen on the basis of chemical yield and purity of product, ease of recovery of uranium[235], simplicity of equipment, and overall time required for processing. Studies of the unit operations in the proposed process and design considerations for a pilot plant and final processing plant are presented in separate reports.[10,11]

3.0 Summary

A process for the production of 30,000-curie batches of barium[140] from Materials Testing Reactor assemblies was developed and successfully demonstrated on a laboratory scale. The barium yield was greater than 97.0% and the product met or exceeded all purity specifications. The process showed good reproducibility and operability with an overall operating time of approximately seventeen hours. The waste solution is suitable for the recovery of the uranium[235] in the "25" solvent extraction process. A

study of the irradiation characteristics of the materials used in the process indicated adequate stability at the anticipated radiation level.

The MTR RaLa Process consists of the dissolution of the assembly in caustic, the recovery of the uranium-barium precipitate from the alumi- nate solution by filtration, and the purification of the barium both by precipitation of barium nitrate from 85% nitric acid and by an ion exchange separation.

Three additional schemes were developed and evaluated for the dis- solution of the assembly and the elimination of the bulk constituents, aluminum and uranium. These schemes utilize a caustic, nitric acid-mer- curic ion, or sulfuric acid-hydrogen peroxide-mercuric ion system for the dissolution step and the precipitation of barium sulfate or barium nitrate for the bulk separation step. It was concluded that these processes were less desirable in terms of equipment simplicity, ease of recovery of ura- nium^{235} from the waste stream, or radiation stability of the required chemicals.

Ion exchange and the precipitation of barium chloride from concen- trated hydrochloric acid were studied as alternate methods for the sepa- ration of barium from the micro-contaminants. The ion-exchange method was selected on the basis of high yield, purity of product, and reliabi- lity.

4.0 Physical Considerations

4.1 Composition of an Irradiated Assembly

The final operating schedule for the MTR reactor had not been fixed at the time the MTR RaLa Process was developed, thus preventing an accu- rate calculation of the composition of the irradiated assemblies to be used in the process. As a result it was necessary to develop a flexible process which could handle one or two assemblies with irradiation times of 12 to 37 days. Assemblies with longer or shorter irradiation periods could be processed with a slightly modified procedure.

An assembly irradiated for 12 days would contain 2.96×10^4 curies of barium^{140} — 0.94 g of barium; 135-204 g of uranium, depending on the amount of uranium^{235} present; and approximately 0.76 g and 4.8 g of stron- tium and rare earths respectively. Irradiation for 20 or 37 days would produce 3.88×10^4 curies of barium^{140} — 1.4 g of barium, or 4.4×10^4 curies — 2.1 g of barium, respectively. The latter figure represents the maximum amount of barium^{140} activity which can be produced in an assembly.[11] Since the consumer's minimum requirements are 3.0×10^4 curies per batch, it will be necessary to process two 12-day assemblies or one 20- or 37-day assembly. From the consumer's viewpoint, the 12-day material is preferable because the shorter irradiation results in a lower mass ratio of barium^{138}/ barium^{140}.

The barium decay scheme

$$Ba^{140} \xrightarrow[12.8 \text{ d}]{} La^{140} \xrightarrow[40 \text{ hr}]{} Ce_{(st)} \qquad (1)$$
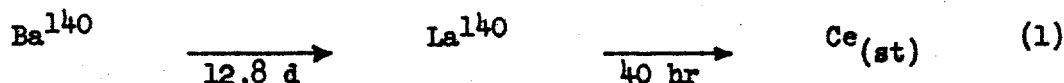
must also be considered in estimating the total curies needed for the production of 3.0×10^4 curies. For all practical purposes, the barium[140] decay amounts to 5% per day. Thus, a 20-day irradiation, equivalent to 3.88×10^4 curies, should be sufficient and would permit a 20% processing loss, although the anticipated losses amount to only 5% for decay and 3% for chemical processing. The assembly will be processed about four hours after it is discharged from the reactor, thus making the initial decay loss negligible.

The total energy produced by radioactivity in the assembly will decrease from 1.3×10^3 kw[29] at discharge to 5.0 kw[11] after four hours of cooling, at which time the barium will represent only 3-5% of the total.

The amount of uranium in an irradiated assembly will vary considerably but will have little bearing on the barium yield in the MTR RaLa Process. Consequently, the development runs were made assuming 150 g of uranium per assembly and no effort was made to investigate other concentrations. The percent uranium loss per run will vary with the total amount of uranium present, but the actual weight loss should be relatively constant. The weight of aluminum was assumed to be 4.37 kg per assembly, which corresponds to the calculated amount remaining after removal of the end boxes.[11] The calculated compositions of assemblies irradiated for 12, 20, and 37 days are listed in Table 1 and a nomograph for the calculation of the specific activity of each fission product at discharge time is given in Figure 1.

4.2 Product Specifications

The product specifications as supplied by the consumer are listed below. The aluminum specification was not stated but was derived from a knowledge of the consumer's process. The quantities represent the minimum barium[140] content and the maximum impurity content per batch.

RaLa Product Specifications

Barium[140]	3.0×10^4 curies
Barium[140] Barium[138] Strontium[89, 90]	2.0 g total (100 curies strontium)
Iron	500 mg
Chromium	10 mg
Nickel	10 mg
Aluminum	100 mg

An additional specification is that the last separation of barium and rare earths be made just prior to shipment and that the shipment be in the consumer's hands within two days. This precaution is necessary to prevent the build-up of a large amount of cerium, thus rendering the product less valuable (see equation (1)). The final step in the MTR RaLa Process, the fuming nitric acid precipitation, provides the necessary separation of barium from lanthanum and cerium.

4.3 Recovery of Uranium

It was assumed that the uranium waste solutions from an MTR-RaLa Process would be combined with the feed solutions in the "25" Process* for the recovery of the enriched uranium. This procedure, however, places serious limitations on the type of chemicals used in the RaLa Process, since the waste solution must be compatible with the "25" solvent-extraction feed. An initial survey indicated that organic chemicals were not acceptable but that moderate amounts of sodium sulfate or sodium nitrate could be tolerated. Solutions of nitric acid were completely satisfactory in that the nitric acid concentration can be lowered to any desired level by evaporation.

One of the processes investigated, the Caustic-Sulfate Process, required the use of 400 moles of sulfate per assembly for the precipitation of barium (see Section 6.0). A sample of the uranium sulfate from this process was run through the "25" Process solvent-extraction cycle. The results showed that the efficiency of uranium extraction was lowered to a dangerous degree when the "25" feed solution contained more than 5% by volume of the sulfate waste solution.[12] In view of its effect on solvent extraction, together with other considerations (see Sections 4.41 and 6.2), the use of sulfate was abandoned in favor of nitric acid.

In the proposed MTR RaLa Process >99.6% of the uranium appears in a nitric acid waste solution from which it is easily recovered. The total uranium loss per assembly in the caustic dissolver solution and caustic wash solution filtrates will vary from 0.44 to 0.82 g depending on the irradiation and recycle conditions (see Table 2). These values correspond to uranium^{235} losses of 0.37 and 0.49 g respectively. It was assumed that it would not be economical to recover so small an amount of uranium from the caustic waste solution.

4.4 Radiation Stability

4.41 Process Chemicals

Versene, a chelating agent with the formula ethylene diamine tetra-acetic acid, was proposed initially as a reagent for the dissolution of[8] barium sulfate in an MTR RaLa Process. Previous experience at the 1500

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*The "25" Process is the process for recovery and decontamination of uranium from MTR assemblies by solvent extraction.[13]

and 15,000-curie (ORNL RaLa Run 44) level had shown no significant decomposition of Versene by radiation. ORNL RaLa Run 45 at the 21,000-curie level, however, showed that Versene was not stable to prolonged irradiation. The Versene solution in this case was subjected to a total of 0.0404 watt-hr/g, of beta radiation, over a period of 13.5 hours during the feed solution pH adjustment and column feed operations. This irradiation caused a rise in pH at the rate of 0.5 pH unit/hr, $\approx$ 0.17 pH unit/milliwatt-hr/g, and resulted in the precipitation of 35% of the barium. Subsequently, the ORNL RaLa Process was revised to replace Versene in the "hot" feed solution with acetate, which had shown a higher degree of radiation stability.[14]

A program was initiated to study the radiation stability of sodium Versenate using a 3000-curie cobalt^{60} source. A synthetic ORNL RaLa Versene feed solution containing barium, strontium, cerium, lead, and nitrate, along with tracer barium^{140}, strontium^{90}, and cerium^{144}, was irradiated at the rate of 2.18 x 10^{-3} watt/g for 66.5 hours. Air, saturated with water vapor, was bubbled continuously through the solution to maintain its oxygen content in equilibrium with the air. At the end of this period, corresponding to a total energy absorption of 0.155 watt-hr/g, 56%, 74.8%, and 42% of the barium, strontium, and cerium, respectively, had precipitated. Other effects on the solution were a rise in pH from 6.3 to 8.5; a rise in nitrite concentration from zero to 0.13 M; and a change in color from water white to yellow.

In a similar experiment two aliquots of a sodium Versenate-sodium nitrate solution were irradiated at different rates and sampled periodically for analysis. A plot of the millimoles of Versene decomposed versus the total amount of energy absorbed indicates that the Versene is decomposed initially at a rate of 0.69 millimole/watt-hr in an 8.40 x 10^{-4} watt/g field and at 0.55 millimole/watt-hr in a 2.18 x 10^{-3} watt/g field. These values are being checked to see if their difference is actually due to the rate of irradiation or to a possible difference in their equilibrium oxygen content. The loss in chelating power of the Versene during irradiation thus accounts for the precipitation of the cations, probably as their carbonates or as oxalates or succinates formed with Versene decomposition products. After 0.2 watt-hr/g of irradiation the concentration of the Versene had decreased by ~60% and its apparent rate of decomposition had approached zero. It has not been determined as yet whether the organic decomposition products are selectively oxidized in the later stages of irradiation and thus protect the Versene or if the decomposition products absorb in the same spectrophotometric range as Versene and are thus mistaken for Versene. The pH of the solutions rose from 6.3 at an approximate rate of 0.06 pH unit/milliwatt-hr/g to the range of 8.5 to 9.5 and then remained constant. The rise in pH is attributed to the formation of weak acids and strong bases (amines) as Versene decomposition products (see Figure 2).

It was concluded that Versene should not be used for the dissolution of barium sulfate in an MTR RaLa Process because of its limited radiation stability. The time required for the pH adjustment of this solution, prior to its use as the ion-exchange column feed, would undoubtedly expose

the Versene to excessive radiation.

The precipitation of barium chloride from ethyl ether-hydrochloric acid is a standard radiochemical separation technique and was used in the ORNL RaLa process at levels up to 4000 curies of barium[140]. A number of RaLa products were black in color, however, rendering the radiation stability of the ethyl ether suspect. It was subsequently shown by I. R. Higgins that irradiation of an ethyl ether-hydrochloric acid solution to 0.14 watt-hr/g by a cobalt[60] source caused the formation of colloidal black decomposition products.[15] Consequently ethyl ether was not considered as a process chemical.

Other process chemicals such as sodium nitrate, sodium hydroxide, and nitric acid have been used extensively for the dejacketing and dissolution of irradiated slugs and were assumed to be essentially stable to radiation.

4.42   Ion Exchange Resin

ORNL RaLa Runs 45 and 46 were studied in detail to determine the radiation stability of Dowex-50 resin under actual process conditions. The solutions entering and leaving the column were analyzed for barium[140], strontium[89], cerium[141, 144], and gross beta. Using these analyses, the average residence time of the activity on the column and the total beta energy absorbed by the column system was calculated. It was assumed[16] that the gamma radiation damage was negligible and that the beta damage was proportional to

$$E \text{ (average)} = (0.4) \, E \text{ (maximum)}. \tag{2}$$

Run 45 contained 12,500 curies of barium[140], 1740 curies of strontium[89], about 1000 curies of lanthanum[140], and 500 curies of cerium[141,144]. The resin system absorbed 0.23 kwh of beta radiation energy per kilogram of oven-dry H^+ form resin, or 0.11 kwh per liter of H^+ form resin, over a period of eighteen hours. Run 46 contained 30,000 curies of barium[140], 1250 curies of strontium[89], about 8000 curies of lanthanum[140], and 700 curies of cerium[141,144], amounting to 0.27 kwh per kilogram of oven-dry H^+ form resin over a period of fourteen hours. The resin capacity loss in the latter case should approximate only 2-4% based on results reported I. R. Higgins[17]. This work showed a resin capacity loss of 10-15%/kwh/kilogram of resin from radiation produced by cerium[144] in column operations or by irradiation of resin in glass ampules by a cobalt[60] source. This work also showed that anion resins are less stable to radiation than cation resins. Consequently anion resins were not considered for use in the MTR RaLa Process.

The irradiation of the resin columns in ORNL Runs 45 and 46 did not impair the efficiency of the systems for barium purification. It is therefore assumed that ion exchange will be suitable for the MTR RaLa Process and will be well within radiation safety limits since the resin irradiation time in this case will be lower by a factor of three than in the ORNL RaLa Process.

The resin column should be charged with new resin for each RaLa run to avoid a build-up of radiation damage.

4.5 Choice of Separation Methods

The MTR RaLa Process can be divided into three major steps: assembly dissolution; separation of barium from the bulk constituents, uranium and aluminum; and separation of the barium from the fission products.

Nitric acid, sulfuric acid, and caustic were studied as reagents for the dissolution of the assembly. Caustic dissolution was selected for the MTR RaLa Process because of its efficiency and because it afforded an excellent method for the separation of the barium from the aluminate solution by filtration.

Precipitation and ion exchange were considered as methods for the separation of the bulk contaminants. The precipitation method was chosen because it provided a fast, efficient separation whereas ion exchange would require large volumes and a relatively long operating time. In addition, the sulfuric acid used for the separation of barium from uranium by cation exchange[18] would not be acceptable in the process used to recover the uranium^{235} (see Section 4.3). From a stability standpoint, there was no certainty that the resin could withstand the tremendous amount of radiation of the dissolver solution where the barium furnishes only 3.5% of the total energy from radioactivity. The precipitation method, however, would be stable to radiation and would eliminate a large fraction of the fission products. Thus the level of radiation would be lowered to the point where it is known that the resin can be used effectively and would permit the use of ion exchange for the succeeding purification step (see Section 4.42).

Ion exchange was selected for the separation of barium from strontium and other fission products. This method is excellent for processing small amounts of material by remote control and produces a pure product in high yield. ORNL RaLa experience has demonstrated the effectiveness of ion exchange for the purification of barium^{140}. Purification of barium by a hydrochloric acid precipitation process was not satisfactory in that the barium loss was high, the separation from strontium uncertain, and the small volumes required would be difficult to handle by remote control (see Section 9.0).

5.0 MTR RaLa Process

The recommended MTR RaLa Process consists of the following steps: (1) dissolution of the assembly in caustic and separation of the aluminate solution from the uranium-barium precipitate by filtration; (2) dissolution of the precipitate in nitric acid and the precipitation of barium nitrate by the addition of fuming nitric acid; (3) purification of the barium by ion exchange; and (4) final purification and volume reduction by a fuming nitric acid precipitation (see flowsheets, Figures 3 and 4, and Table 2).

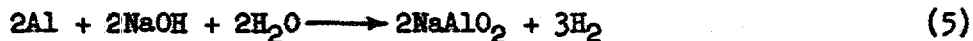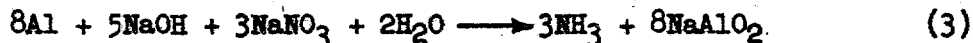### 5.1 Assembly Dissolution

5.11 Dissolution Rate

Dissolution of assembly sections in sodium hydroxide and sodium nitrate produces a very vigorous reaction. The fast evolution of gas causes foaming and a resultant increase in solution volume of about 100%. It was necessary to control the reaction by adding the caustic slowly over a period of 1/2 hour. Dissolution was complete in 1 to 2 hours when the mole ratio of NaOH/Al was 1 or greater. Any substantial reduction in this ratio resulted in incomplete dissolution and unstable solutions. Only the higher concentrations of aluminum (1.8 to 5.0 M) were considered in this study in order to limit the dissolver solution volume and consequently the total uranium loss as soluble uranium.

5.12 Off-gas Composition

Sodium nitrate is added to the dissolver solution to oxidize the hydrogen formed during the dissolution of aluminum by sodium hydroxide and thus reduce the explosion hazard. The following equations describe the reactions involved:

$$8Al + 5NaOH + 3NaNO_3 + 2H_2O \longrightarrow 3NH_3 + 8NaAlO_2 \qquad (3)$$

$$2Al + 3NaNO_3 + 2NaOH \longrightarrow 3NaNO_2 + 2NaAlO_2 + H_2O \qquad (4)$$

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2 \qquad (5)$$

A maximum of 60.7 moles of ammonia would be evolved per assembly if the reaction proceeded according to equation (3) alone. Actually the reaction is a combination of the three equations.

The composition of the off-gas was studied as a function of the initial mole ratios of Al : $NaNO_3$: NaOH and the final Al concentrations. It was found that the amount of hydrogen in the off-gas varied directly with the initial NaOH concentration at constant Al and $NaNO_3$ concentrations; and indirectly with the initial $NaNO_3$ concentration at constant Al and NaOH concentrations. At the recommended flowsheet conditions of mole ratios of Al : $NaNO_3$: NaOH of 1 : 0.5 : 1 at 5.0 M Al, the hydrogen evolution did not exceed 2 ml per gram of MTR assembly (see Figure 5). This value agrees very well with that reported by A. T. Gresky[19] for the caustic dissolution of P-10 slugs. At this rate, the dissolution of one assembly would produce about 9.0 liters of hydrogen, which is considered well within safe limits.

The ratios of the final concentrations of NO_2^- to Al were plotted as a function of sodium molarity as a convenient method for presenting several variables. The curves show that the fraction of the aluminum dissolved by equation (4) varies directly with the initial $NaNO_3$ concentration at constant Al and NaOH concentrations, and indirectly with the initial NaOH concentration at constant Al and $NaNO_3$ concentrations. In plotting the percent of aluminum dissolved by equation (4), it was assumed that the ratio

5.21 Filtration

Without Filter Aid

The solutions filtered rapidly and did not plug an "H" stainless steel filter but it was necessary to recycle the solution to obtain a clear filtrate. The uranium loss was 0.5 - 1.0%.

Celite Filter Aid

Celite filter aid was tried in an effort to reduce the uranium loss and eliminate the recycle. The caustic solution attacked the Celite, however, making its use impractical.

Asbestos Filter Aid

Asbestos, with the formula $Ca_2Mg_5(OH)_2(Si_4O_{11})_2$, proved to be a satisfactory filter aid. It is reasonably stable in caustic solutions, possesses good filtration characteristics, and is stable to heat. The latter point is of interest because of the large amount of heat derived from the radioactive precipitate. The system cannot tolerate too great an addition of calcium or strontium, and the barium addition should not exceed ~0.2 g. The following series of tests was run to determine the impurities that would be added to the RaLa system from the use of this filter aid: A sample of medium-fiber, acid-washed, and ignited asbestos was refluxed for three hours with 3.0 M caustic in a stainless steel container and subsequently leached for three hours with boiling 6 M nitric acid as a pretreatment purification step. The leachings were then repeated to simulate process conditions. The asbestos samples were dried for twenty-four hours at 110°C and weighed before and after the second caustic and acid treatments, and the total weight loss was determined as ~3.0%. The caustic solution contained 0.25 and 22.6% of the weight of the asbestos as silica and total alkaline earths, respectively, and the acid leach 0.6 and 0.03%, respectively. Barium was not detected by gravimetric analysis in either solution. These results indicate that the amount of impurities derived from the asbestos would not be excessive, since only those contained in the acid solution enter the RaLa system.

The efficiency of asbestos as a filter aid was determined on the basis of uranium loss as solids and on filtration rate. The solid uranium loss was defined as that uranium which passed through the asbestos-"H" stainless steel filter but which was retained by No. 42 quantitative paper. It was shown that an asbestos precoat was necessary but that 1.28 g of asbestos precoat per square inch of filter was no more efficient than 0.64 g/in.^{2} for retaining uranium particles. The solid uranium loss was lowered by a factor of 4 by increasing the amount of filter aid from 2.5 to 5.0 g/liter, but any further increase resulted in an excessive loss in filtration rate. The average solid uranium loss for twelve runs using 0.64 g/in.^{2} of precoat and 5.0 g/liter of asbestos filter aid was 0.06% with individual variations ranging from 0-0.1%. Increasing the Al concentration from 3.6 to 5.0 M and variations in the mole ratio of Al : $NaNO_3$: NaOH made little difference in the solid uranium loss.

11.0 Bibliography

1. Baldwin, W. H., Savolainen, J. E., The Development of a Chemical Process for the Preparation of Ba^{140}, MonN 330

2. Eister, W. K., Semi-Works Development of the RaLa Process, ORNL-231

3. Culler, F. L., Goeller, H. E., Unger, W. E., RaLa Study Preliminary Report #1, ORNL Central Files #49-4-38

4. Unger, W. E., Design Considerations in RaLa Processes, ORNL-622

5. Blanco, R. E., Laboratory Development of an Ion Exchange RaLa Process, ORNL-620

6. Blanco, R. E., Kibbey, A. H., Laboratory Development of the Versene Process for the Purification of Radiobarium by Ion Exchange, ORNL-625

7. Higgins, I. R., ORNL RaLa Pilot Plant Development, ORNL-621

8. Higgins, I. R., Blanco, R. E., Unger, W. E., Preliminary Demonstration of RaLa Ion Exchange Processes at the Kilocurie Level, ORNL-623

9. Vaughan, R. H., RaLa Production - Overall Economic Survey, ORNL Central Files #51-8-264

10. Arehart, T. A., MTR RaLa Unit Operation Studies, ORNL-1247

11. Unger, W. E., et al, MTR RaLa Design Report, ORNL-1150

12. Ferguson, D. E., Laboratory Status Report, 6-8-51
         Chemical Technology Division ORNL-FLS #734

13. Bruce, F. R., The Laboratory Development of a Continuous Solvent Extraction Process for the Recovery of U^{235}, ORNL-343

14. Blanco, R. E., RaLa Development, QUARTERLY REPORT, ORNL Central Files #51-11-161

15. Higgins, I. R., Laboratory Status Report, 9-21-51
         Chemical Technology Division ORNL Central Files #51-9-118

16. Marinelli, L. D., Brinckerhoff, R. F., Hine, G. J., Reviews of Modern Physics 19, 25 (1947)

17. Higgins, I. R., Ion Exchange Studies, QUARTERLY REPORT, ORNL Central Files #51-11-56; Homogeneous Reactor - Continuous Fuel Processing, QUARTERLY REPORT, ORNL Series FLS-793

Bibliography (Cont'd)

18. Schubert, J., Boyd, G. E., Cohn, W. E., Davies, T. H., et al, The Extraction, Concentration, and Decontamination of Ba^{140} from Uranyl Nitrate Solutions by an Adsorption Process, CN-2563

19. Gresky, A. T., Recovery of Nitrogen Oxides and Rare Gas Fission Products from the Nitric Acid Dissolution of Irradiated Uranium, ORNL-1208

20. Burns, R. E., Giles, H. S., Holm, C. H., Moore, R. L., Leitz, F. J., Caustic Dissolution of p-10 Slugs, HW-18413

21. Granquist, D. P., Sege, G., "25" Process Low Volume Hexone Flowsheet, HW-18135

22. Tompkins, E. R., Khym, J. X., Cohn, W. E., J. Am. Chem. Soc., 69, 2769 (1947)

23. Spedding, F. H., Discussions of the Faraday Society No. 7, 214-231, 1949

24. Blanco, R. E., Higgins, I. R., Separations of Fission Products from Aluminum Waste Solutions by Ion Exchange, ORNL-301

25. Blanco, R. E., RaLa Development, QUARTERLY REPORT, ORNL Central Files #52-2-192

26. Seidell, A., Solubilities of Inorganic and Metal Organic Compounds, Vol. I, 3rd ed., D. Van Nostrand Co., Inc., New York, 1940, p. 183-184

27. Ayres, J. A., McCullough, G. E., McKeehan, W. F., Simon, R. H., Recovery of Aluminum Nitrate from Redox Aqueous Waste Streams, KAPL-213

28. Gillette, P. R., Activity of Fission Products, HW-17415

29. Goeller, H. E., The Cooling of Irradiated 25 MTR Fuel Assemblies and Its Effect on 25 Inventory in the MTR Project, ORNL-611

30. Pannell, J. H., MTR RaLa Process Development - HCl Precipitation Process, ORNL-Central Files #52-1-189

Table 1

Approximate Composition of an Irradiated MTR-Assembly

tions:

U^{235} content as a function of irradiation time = $140 e^{-\phi\sigma t}$ gm/assembly

Radioactive fission product mass(gm)=$\dfrac{(140)(\phi)(\sigma)(0.86)(\text{Fission Yield})(\text{At.Wt})(e^{-\phi\sigma t}-e^{-\lambda t})}{(\lambda-\phi\sigma)(235)}$

Stable fission product mass (gm) = $\dfrac{(140)(\text{At.Wt})(\text{Fission Yield})(0.86)(1-e^{-\phi\sigma t})}{(235)}$

$(\phi)(\sigma)$=0.01105/sec; ϕ=neutron flux; σ=U^{235} cross section; λ=decay constant; 0.86=fraction of U^{235} fissioning; fission yields as reported by P. R. Gillette.[28]

oactive Energy: At discharge = 1.3 x 10^3 KW[29] ?
4 hrs cooling = 5.0 KW[11]
24 hrs cooling = 1.48 KW

mptions: (1) MTR power level = 30,000 KW
(2) With the exception of Ba^{140}, Sr^{89}, Ce^{141}, and I^{131}, the decay chains begin and end with the first long-lived product.

Constituent		Grams/Assembly		
		Irradiation Time (Days)		
		12	20	37
	Ba^{138}	0.54	0.87	1.5
	Ba^{140}	0.40	0.53	0.6
	$Sr^{88,89,90}$	0.76	1.2	2.0
	$Ce^{140,141,142,144}$	1.6	2.5	4.4
Rare Earths:	(Other than Ce; includes $La^{139,140}$ and Y^{91})	3.2	5.2	8.9
Inert Gases:	$Kr^{83,84,86}$	0.18	0.28	0.48
	$Xe^{131,132,134,136}$	1.1	1.9	3.3
Alkali Metals:	$Rb^{85,87}$	0.23	0.37	0.62
	$Cs^{133,135,137}$	1.4	2.2	3.8
Halogens:	$*Br^{81}$	0.008	0.012	0.021
	$I^{127,129,131}$	0.21	0.28	0.35
Zinc Group:	$Zr^{91,92,94,95,96}$	1.4	2.3	3.9
	Nb^{93}	0.36	0.58	0.98
	$*In^{115}$	<0.001	0.001	0.002
Platinum Metals:	$Ru^{101,102,103,104,106}$	0.92	1.5	2.5
	$*Pd^{105}$	0.087	0.14	0.24
Arsenic Group:	$Se^{78,79,80,82}$	0.020	0.032	0.055
	$Te^{126,127,128,129,130}$	0.24	0.39	0.66
	$Mo^{97,98,100}$	1.1	1.7	2.9
	$*Sb^{121}$ and $Sn^{117,118,119,120,122,123,124,125}$	0.010	0.016	0.028
	$*Cd^{111,112,113,114,116}$	0.004	0.007	0.012
	$*Ag^{109}$	<0.002	0.003	0.005
	$*Tc^{99}$	0.35	0.56	0.96
	U^{235} [29]	122.6	112	92.4
	$U^{234,236,238}$	12.4-81.1	13.8-82.5	16.6-85.3
	Al	4,370	4,370	4,370
	Si (from welding flux)	35	35	35

ot included in synthetic experimental solutions.

SECRET

Table 2

Operating Flow Rates for the MTR RaLa Ion Exchange Process

See Flowsheet, Figure 4.

Solution	Volume (liters)	Flow Rate (ml/min)	Total Time (hrs)	Average Resin Irradiation Time (hrs)
(1) "Hot" Feed	20	550	0.61	0.32
(2) Wash - H_2O	2	550	0.06	0.06
(3) Rare Earth & Al Elution: 0.5 M Na Citrate pH 3.2	22	260	1.42	∼1.42
(4) Wash: A. H_2O B. H_2O	2.5 7.5	260 550	0.16 0.23	0.16 0.23
(5) Sr Elution: 0.07 M Na Versenate pH 6.3	12.0	260	0.77	∼0.77
(6) Wash: A. H_2O B. H_2O	2.5 7.5	260 550	0.16 0.23	0.16 0.23
(7) Na Elution: 2.0 M HNO_3	2	550	0.06	0.06
(8) Product Elution: A. 9.0 M HNO_3 B. 9.0 M HNO_3	5 10	425 100	0.20 1.67	0.10 Negligible
Total:	93	---	5.57	3.51

Table 3

Distribution of Fission Products in the MTR RaLa Process

Conditions:

20g transverse sections of an MTR RaLa assembly were irradiated for sixteen hours in the ORNL pile and processed after five hours.

Carrier fission products were added to the uranium dissolver solution corresponding to 12- or 37-day irradiations in the MTR reactor (see Table 1).

For process conditions see flowsheets, Figures 3 and 4 and Table 2. 12 and 37 day results are reported separately only when significantly different.

% of Total Initially Present at Process Time

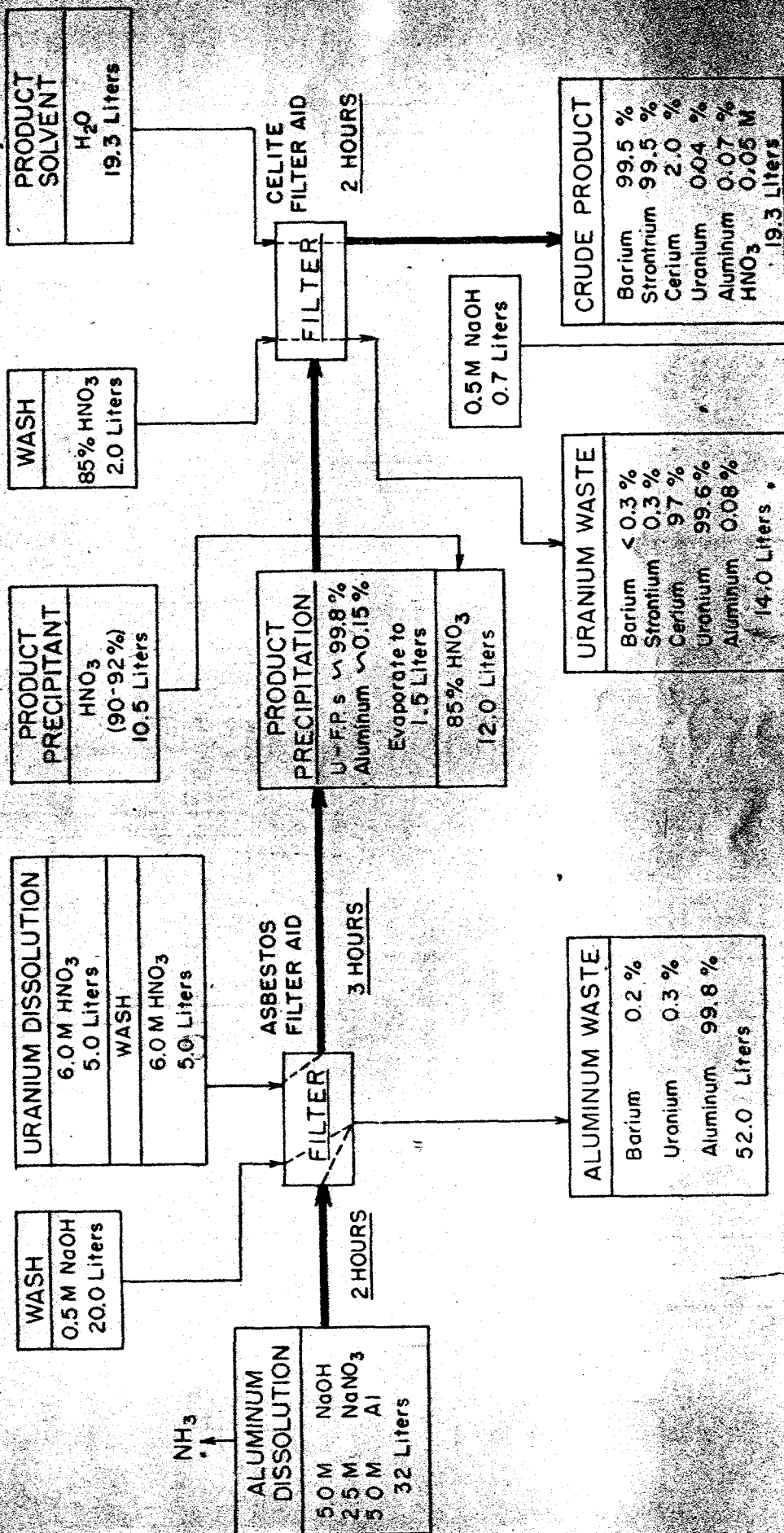| Process Step:	Gross β	Ba	Sr	Zr	Cb	Ru	Cs	I	Total R.E.	U	Al
Dissolution: Caustic Waste	2.58	0.2	0.2	-	-	-	-	1.0	*0.1 ~0.2	0.3	>99.8
1st Fuming HNO₃ Precipitation: Uranium Filtrate	93.92	0.3	0.3	~99.9	~99.6	~99.7	~99.3	96.9	*97.9 ~74.8	>99.6	0.08
Ion Exchange: Combined Wastes	-	0.7	>99.1	0.001	0.4	0.06	0.4	1.9	*1.9 24.5	<0.01	0.07
2nd Fuming HNO₃ Precipitation: Final Barium Product	-	>97	<0.3	0.005	0.0	0.0	0.0	0.1	*0.005 <0.03	<0.0003	<0.0006

*12-Day Irradiation

Figure 3

FLOWSHEET: MTR-RaLa PROCESS-Part 1
PREPARATION OF CRUDE BARIUM140 BY THE CAUSTIC-NITRATE PROCESS

BASIS: 1 MTR Assembly

162 Moles Aluminum
0.65 Moles Uranium
6.8×10^{-5} Moles Ba
12 day irradiation

PRODUCT SOLVENT

H_2O
19.3 Liters

CELITE FILTER AID
2 HOURS

CRUDE PRODUCT

Barium	99.5 %
Strontium	99.5 %
Cerium	2.0 %
Uranium	0.04 %
Aluminum	0.07 %
HNO_3	0.05 M
	19.3 Liters

TO ION EXCHANGE
(see part II figure 4)

WASH

85% HNO_3
2.0 Liters

FILTER

0.5 M NaOH
0.7 Liters

PRODUCT PRECIPITANT

HNO_3 (90-92%)
10.5 Liters

PRODUCT PRECIPITATION

| U-F.P.s ∽99.8% |
| Aluminum ∽0.15% |
| Evaporate to 1.5 Liters |
| 85% HNO_3 |
| 12.0 Liters |

URANIUM WASTE

Barium	< 0.3 %
Strontium	0.3 %
Cerium	97 %
Uranium	99.6 %
Aluminum	0.08 %
	14.0 Liters

TO "25" PROCESS FOR URANIUM RECOVERY

ASBESTOS FILTER AID
3 HOURS

URANIUM DISSOLUTION

6.0 M HNO_3	5.0 Liters
WASH	
6.0 M HNO_3	5.0 Liters

FILTER

ALUMINUM WASTE

Barium	0.2 %
Uranium	0.3 %
Aluminum	99.8 %
	52.0 Liters

2 HOURS

WASH

0.5 M NaOH
20.0 Liters

ALUMINUM DISSOLUTION

NaOH	5.0 M
$NaNO_3$	2.5 M
Al	5.0 M
	32 Liters

NH_3